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Increased zinc concentrations in the Canadian Arctic air

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ABSTRACT

Long–term time trends for heavy metals in Canadian arctic surface air were studied recently. Different from the continuing decrease for other metals, such as cadmium and mercury, from 1973 to 2000, zinc concentrations decreased from 1973 to the mid–1980s and then increased again at Resolute (74.7°N, 95.0°W). Its concentrations in the surface air increased from less than 10 ng m^{-3} in the mid–1980s winters to more than 20 ng m^{-3} in the late 1990s winters. A sharper increasing trend was found at another arctic site, Coral Harbour (64.2° N, 83.3° W), where Zn increased from about 10 ng m^{-3} in air in the early 1970s to more than 100 ng m^{-3} in late 1990s. The increase was also recognized at two sub–arctic sites, Churchill (58.8° N, 94.1° W) and Moosonee (51.3° N, 80.6° W), but not in more southerly sites like Ottawa (45.3° N, 75.7° W) and Windsor (42.3° N, 83.0° W). The possible reasons which led to the Zn increase in the north are discussed in this paper.

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1. Introduction

Arctic air pollution has been studied extensively. Many research activities were conducted on the composition, origin and transport of the "arctic haze" and its health impacts on arctic peoples and the ecosystems. Reviews (Barrie, 1986; Pacyna, 1995; Lockhart, 1995; Muir et al., 1999; Braune et al., 1999; Van Oostdam et al., 1999) and assessment report of international program on arctic pollution (AMAP, 1998) identified the lack of information on the long–term time trend of pollutants like heavy metals as one of the most important knowledge gaps in the arctic pollution studies. We studied the time trends of some heavy metals (Cd, Hg, and Zn) in the surface air of Canadian Arctic using the well archived air particulate samples collected weekly during 1973 and 2000 by the Canadian National Radiological Monitoring Network (CNRMN) of Health Canada. Results for Cd and Hg have been published elsewhere (Li et al., 2003; Li et al., 2009).

The monitoring of heavy metals in Norwegian Arctic air showed a decrease in Zn concentration during the beginning of the 1980s and the beginning of the 1990s at Ny Alesund (Pacyna, 2010). However, snow core analyses conducted by Boutron and his colleagues (Boutron et al., 1991; Savarino et al., 1994) indicated the increased Zn deposition flux in the late 1980s after the early decrease in the snow core samples collected from the Geenland summit. Study on surface snows collected from Agassiz ice cap showed that Zn concentration in 1992 winter–spring snow is higher than that of 1990 and 1988 (Cheam et al., 1998). This paper reports the observations on the long–term time trend for Zn in the Canadian arctic air.

2. Experimental

Surface air particulate samples from Resolute (74.7° N, 95.0° W), Coral Harbour (64.2° N, 83.3° W), Churchill (58.8° N, 94.1° W), Moosonee (51.3° N, 80.6° W), Ottawa (45.3° N, 75.7° W), Toronto (43.6° N, 79.4° W) and Windsor (42.3° N, 83.0° W) (Figure 1) were collected weekly using a standardized sampling method of glass micro–fiber filters by CNRMN between 1973 and 2000. The descriptions on sampling, sample preparation and determination were reported in detail in Li et al. (2003). In summary, one weekly sample for each winter month (December, January, February and March) from a specific site was selected and analyzed. For each analysis, a portion of the filter, which is equivalent to about 350 m^3 air, was cut and leached with HNO_3 and H_2O_2. HNO_3, H_2O_2 and H_2O (18 MΩ) used in the experiments were in high purity. All of the preparations were conducted in a clean laboratory. Procedural blanks and filter blanks were analyzed together with the samples. These experiments showed that there was no significant contamination with Zn during the sampling, the subsequent handling and the sample preparation processes.

The samples were analyzed by ICP–MS (ELAN 6000, Perkin Elmer Sciex, Concord, Ontario). ^{67}Zn (natural abundance, 4.1%) was selected for Zn analysis since other isotopes would suffer mass interferences. For ^{67}Zn, there are still some possible interference, such as $^{134}Ba^{2+}$, $^{134}Xe^{2+}$, $^{32}S^{35}Cl^{+}$, $^{35}Cl^{16}O^{16}O^{+}$ and $^{34}S^{16}O^{16}O^{1}H^{+}$, but compared to the Zn concentrations in the samples, these interferences are negligible. NIST SRM 1648, an urban air particulate reference material, was leached and measured in the same manner to check the leaching efficiency. The experimental

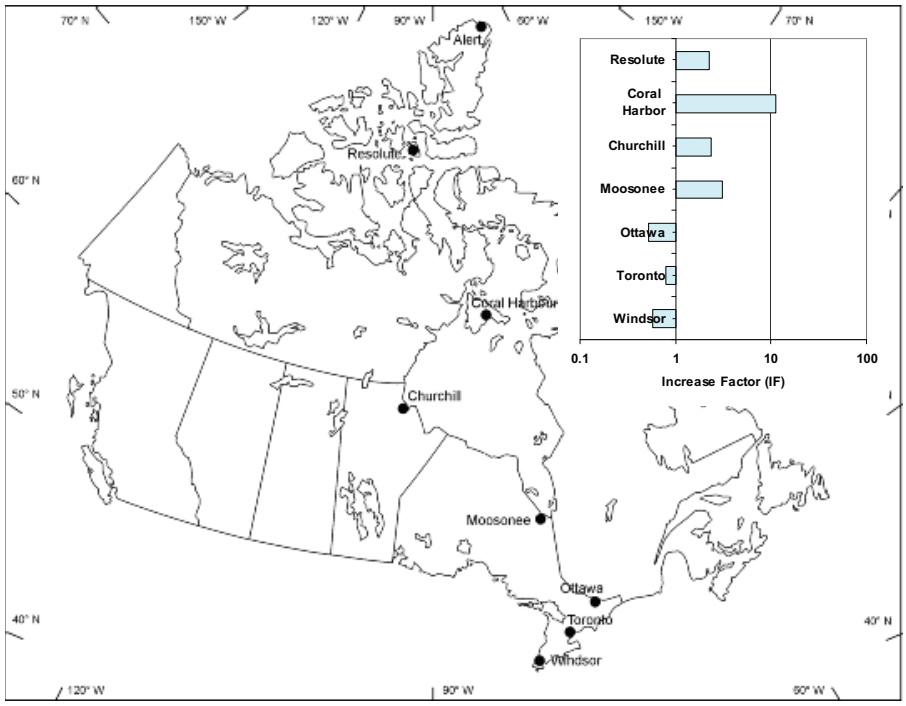

Figure 1. *Sampling locations and latitudinal variation of Increase Factors (IF) for Zn in surface air (IF = $[Zn]_{2000}$ / $[Zn]_{1973}$) of Canada.*

value of 4 320 ± 150 mg kg^{-1} is a little lower but very close to the certified value of 4 760 ± 140 mg kg^{-1} for Zn concentration in SRM 1648, indicating an acceptable leaching efficiency (91%). In this study, we did not correct the observed Zn concentrations in the samples for the leaching efficiency.

3. Results and Discussion

The Resolute station (74.7° N, 95.0° W, 63.8 m) is located on Cornwallis Island and the Coral Harbor station (64.2° N, 83.3° W, 59 m) is located on Southampton Island, Nunavut, Canada (Figure 1). Their high latitudes and low elevations make them ideal for the study of air pollution in the Canadian arctic. Figure 2 presents the time trend of average Zn in the winter surface air at Resolute for 28 winters (2a) and Coral Harbor for 9 winters (2b), with polynomial trend–lines. The slight decrease in the 1970s and the following gradual increase at Resolute are obvious even though large inter–annual fluctuations were observed for some winters. The increase at Coral Harbor is more significant, which reached more than 100 ng m^{-3} in the late 1990s, from about 10 ng m^{-3} in the early 1980s. The large fluctuations observed at both Resolute and Coral Harbor have resulted from the real differences in Zn between the samples collected from different periods of the same year. Large fluctuations in Zn concentrations in snow cores were also encountered in the analyses of snow cores from Greenland summit and Agassiz ice cap (Savarino et al., 1994; Cheam et al., 1998). Measurements of particulate matter on the filter samples showed a decreased particulate matter concentration at Resolute and a constant concentration at Coral Harbor during the past 30 years (Li et al., 2003). So, the increase in Zn was not caused by the increase of particulate matter.

A few filter samples selected from 5 more southerly sites in Canada were analyzed to compare Zn in the air particulates collected in the beginning and the end of the time series of archived samples. The increase in Zn was found at two sub–arctic sites, Churchill (58.8° N, 94.1° W) and Moosonee (51.3° N, 80.6° W), but not in the more southerly sites like Ottawa (45.3° N, 75.7° W) and Windsor (42.3° N, 83.0° W). Figure 1 shows the latitudinal variation of the increase factors (IF, defined as the ratio of average Zn for the winter 2000 over that for 1973) in this north–south transect between longitudes 75° W and 83° W. Zn increased in the sub–arctic sites by a similar factor as at Resolute between 1973 and 2000 while decreased almost by a factor of 2 in Ottawa and Windsor.

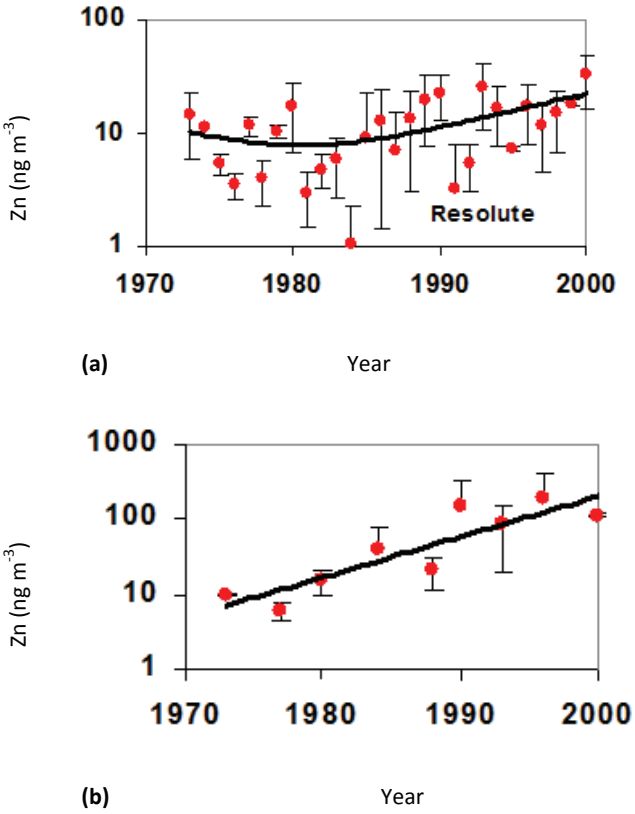

Figure 2. *Time trend of Zn in the Canadian arctic air at Resolute and Coral Harbor:* ***(a)*** *average concentrations of Zn in the winter at Resolute;* ***(b)*** *average concentrations of Zn in the winter at Coral Harbor.*

Natural sources, such as windborne soil particles, wild forest fires, biogenic processes and volcanic emissions contribute about 45 000 tons year^{-1} of Zn to the atmosphere (Nriagu, 1989), which is equivalent to about 34% of anthropogenic emissions of Zn to the atmosphere in the beginning of the 1980s (132 000 tons year^{-1}) (Nriagu and Pacyna, 1988) and about 87% of that in the mid–1990s (52 000 tons year^{-1}) (Pacyna and Pacyna, 2001). The natural emissions should not have changed much in the past 30 years. Climate change like global warming may have led to enhanced Zn emissions from some natural sources to the air; however, such an increase, if it has occurred, should be very small. Moreover, if the natural emissions have really contributed to the increase of Zn in the north, a similar contribution to the south would be expected.

Anthropogenic emissions contributed about 75% of total Zn release to the air in the world in the beginning of the 1980s (Nriagu and Pacyna, 1988; Nriagu, 1989). Table 1 shows the global emissions of Zn to the air from major anthropogenic sources in the beginning of the 1980s and the mid–1990s, where a significant drop in total emissions (by a factor of 2.5) is presented. The latitudinal variations in IF (Figure 1) exclude the hypothesis that the elevated Zn in the Canadian Arctic air was input by fuel combustions and waste incinerations in North America since most of the emissions from these activities were generated in the populous south rather than in the arctic area. Among various anthropogenic sources, the primary production of non–ferrous metals is the most important. The primary production of Zn itself contributed 50–70% of total anthropogenic Zn emissions in the beginning of the 1980s and about 70% of that in the mid–1990s. Table 1 also shows a considerable reduction in Zn emissions from non–ferrous metal production in the world.

Eurasia was traditionally considered as the most important source region for trace metals in the arctic air (Barrie and Hoff, 1985; AMAP, 1998). The northward air current from Siberia in the winter (Wendland and Bryson, 1981) could bring polluted air mass to the Arctic from southern industrial areas via long–range transport (LRT). Many studies, including modeling, investigations showed that the Canadian Arctic was under the impact of polluted air mass from Eurasia (Iversen, 1984; Barrie and Hoff, 1985). Kola Peninsula (67° N), Pechora Basin (65° N) and Norilsk area (69° N) were referred most frequently when talking about heavy metal pollution in the arctic air since they are so near the Arctic and there are many non–ferrous metal smelters in these regions. However, the emissions of Zn to the air from these areas (498 tons) accounted for only a few percent of total Zn emissions to the air in the former USSR (20 800 tons) in 1979 (Pacyna et al., 1995). The production of non–ferrous metals in Russia did not increase in the past decade (AMAP, 1998), and this may apply to the above mentioned areas. Therefore, it seems hard to attribute the increased Zn in the Canadian Arctic air to the emissions from these areas.

LRT could bring Zn–bearing particles to the Canadian Arctic not only from the above Russian Arctic areas (north of 65°N), but also from more southerly regions in former USSR and even from other regions like Northern China. In Urals (55° N), Donetsk area (48° N), Kuznetsk area (53° N) and Fergana area (40° N), the emissions of Zn to the air were much higher than those in the Russian Arctic areas in 1979 (3 920, 2 520, 8 830 and 4 550 tons, respectively (Pacyna et al., 1995). Since the beginning of 1980s, production of many industrial goods in China increased sharply (Table 2, the data in the brackets of the production columns represent the world percentages), the estimated Zn emissions increased accordingly (Table 2, the data in the brackets of the emission columns represent the world percentages). Zn–bearing pollution from the USSR regions mentioned above and China would be brought to the Canadian Arctic eventually via LRT and contribute significantly to the Zn budget in the Canadian Arctic air; however, the increase in Zn emissions in China would not compensate the overall decrease in the world so that the observed increase in Zn concentration in Canadian Arctic air could not be explained by the increase of Zn emissions in China.

Table 1. *Global emissions of Zn to the air from major anthropogenic sources in the beginning of 1980s and mid-1990s (after Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001)*

	Zn Emissions (tons year^{-1})	
Sources	**1983** [a]	**1995** [b]
Fuel combustion [c]	3 102 - 23 416	8 551
Non-ferrous metal production	51 025 - 93 828	37 112
Steel and iron production	7 100 - 31 950	1 923
Cement production	1 780 - 17 800	2 424
Waste disposal [d]	2 950 - 8 850	1 755
Others [e]	4 294 - 17 633	-
Total	70 250 - 193 500	52 000
Median	132 000	

[a] *After Nriagu and Pacyna (1988)*

[b] *After Pacyna and Pacyna (2001)*

[c] *Including stationary and traffic fossil fuel (oil and coal) combustion*

[d] *Including incineration of municipal waste and sewage sludge*

[e] *Including fertilizer usage, wood combustion etc.*

Table 2. *Productions of industrial goods [a] (x10^6 tons year^{-1}) and estimated emissions of Zn (tons year^{-1}) (with percentages of the world total productions or emissions in the brackets) in 1986 and 1995 in China*

	Emission factor	1986		1995	
	(gram ton^{-1}) [b]	Production (%) [a]	Emission (%) [c]	Production (%) [a]	Emission (%) [c]
Coal	1.5	894 (27)	1341	1 361 (36)	2042
Zn	10 000	0.34 (5)	3 400 (6)	1.08 (16)	10 800 (32)
Cu	500	0.42 (4)	210 (4)	1.08 (10)	540 (15)
Primary Pb	80	0.20 (7)	16 (5)	0.61 (21)	49 (29)
Steel & iron	3.0	103 (9)	309 (2)	201(16)	603 (31)
Cement	2.0	166 (17)	332 (4)	401 (29)	802 (33)
Total [d]	-	-	5 608 (5)	-	14 836 (29)

[a] *United Nations, 1997, Industrial Commodity Statistics Yearbook 1995, United Nations, New York. Data in the brackets indicate the percentages of the world total productions. Only hard coal production data are available for China. Total productions of Zn and Cu, and primary production of Pb in China and the world were used here. The sums of steel-making pig iron and crude steel productions were used.*

[b] *Defined as amounts (grams) of metal released per unit (metric ton) of metal produced. Emission factors cited here are from Pacyna and Pacyna, 2001. The emission factors for coal combustion, steel and iron production and cement production are world average, while the emission factors for primary productions of Cu, Zn and Pb are the average in countries in Asia, Africa and Southern America.*

[c] *Emission data for China were calculated from the production data and the emission factors. Data in the brackets indicate the percentages of the world total emission from the indicated sectors. The world emission data for 1983 were used instead of those for 1986. There are no data for world total Zn emissions from coal combustion for both 1983 and 1995. The world total emissions of Zn in 1983 and 1995 from productions of Zn, Cu, Pb, steel and iron, and cement were cited from Pacyna and Pacyna, 2001, where data for 1983 were calculated from Nriagu and Pacyna, 1988. The world total emission data for steel and iron production and cement production were for 1994 instead of 1995.*

[d] *The total Zn emissions in China are the sums of the above listed items for 1986 and 1995, respectively; while the total emissions of the world for the two years are from Pacyna and Pacyna, 2001, where data for 1983 were calculated from Nriagu and Pacyna, 1988.*

Mining and smelting would emit considerable amounts of heavy metals to the local atmosphere. The fine dust from mining and emissions from regional smelting in the Canadian Arctic area would cause local air pollution in heavy metals such as Zn. Arctic mining has caused pollution to some local ecosystems. For example, in Greenland, the Black Angel Pb/Zn Mine (closed in 1990) led to Cd pollution to the coastal water and to the marine and terrestrial animals (AMAP, 1998). Many Zn mines, Pb/Zn and Pb/Zn/Cu mines were developed in the Canadian Arctic. The Polaris Pb/Zn Mine (Cominco Ltd. and Teck Corp., 75.3° N, 96.3° W, Nunavut) is within 100 km of our sampling station at Resolute Bay. The metallurgical complex at Flin–Flon (HBM & S Co. Ltd, 54.8° N, 101.9° W, Manitoba) is only 600 km west of our Churchill sampling station. The Fonderie Horne smelter (Noranda Inc., 48.3° N, 78.5° W, Quebec) is located 300 km south of our Moosonee sampling station. The emissions from all of the above mines or smelters may input a heavy metal burden to our corresponding sampling stations. However, there are not mines or smelters within 600 km of our Coral Harbor sampling station on Southampton Island, where the sharpest increase in Zn concentration in the air during the past 30 years (Figure 1) was observed. The Nanisivik Zn/Pb/Ag Mine (Nanisivik Mine Ltd, 73.0° N, 84.5° W, Nunavut) is 1 000 km north of it and the Raglan Ni/Cu/Co Mine (Ralgan Mines Ltd, 62° N, 75° W, Quebec) is more than 600 km south of it. These prevent us from postulating that the Zn increases observed in this study have resulted from arctic mining.

In summary, Zn concentrations have increased since the mid–1980s in the Canadian Arctic and Sub–Arctic air, while decreased in the southern more populous regions. The increases in the north could not be explained by the natural emissions, waste incinerations and fuel combustions in North America, arctic mining activities, and non–ferrous metal productions in Russian Arctic areas, and are unlikely by long range transportation that bring Zn–bearing particles to the Canadian Arctic from further south. The actual reasons for such an increase remain unexplained.

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